

1971

# I. Varied-Portions Approach to Second-Order Properties. II. Long-Range Interaction of Helium Atoms; Study of Three and Four Electron Correlation effects.

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I. VARIED-PORIONS APPROACH TO SECOND-ORDER PROPERTIES

II. LONG-RANGE INTERACTION OF HELIUM ATOMS; STUDY OF  
THREE AND FOUR ELECTRON CORRELATION EFFECTS

A Dissertation

Submitted to the Graduate Faculty of the  
Louisiana State University and  
Agricultural and Mechanical College  
in partial fulfillment of the  
requirements for the degree of

Doctor of Philosophy

in

The Department of Chemistry

by  
Bert R. Riemenschneider  
B.A., Rice University, 1962  
December, 1971

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## ACKNOWLEDGMENT

The author wishes to express his sincere appreciation to Professor Neil R. Kestner for his patience and guidance. Gratitude is also extended to the other members of the theoretical group, especially to Bijan K. Rao and Joseph T. Broussard for many valuable discussions. Immeasurable gratitude is also due to his wife, Sue, and his daughter, Terry, for their encouragement, patience, and long-suffering. Many thanks also go to his parents without whose encouragement and assistance this goal would not have been attained.

Financial assistance is gratefully acknowledged from the National Science Foundation for a research assistantship under a grant to the Louisiana State University. The help of the Dr. Charles E. Coates Memorial Fund of Louisiana State University Foundation donated by George H. Coates is also appreciated.

## TABLE OF CONTENTS

ACKNOWLEDGMENT. . . . .	ii
LIST OF TABLES. . . . .	v
ABSTRACT. . . . .	vi

### PART I: VARIED-PORCTIONS APPROACH TO SECOND-ORDER PROPERTIES

I. PROPERTIES INVOLVING ONE-ELECTRON OPERATORS . . . . .	1
APPENDIX I: Varied-Portions Approach to Second-Order Properties Involving One-Electron Operators. . . . .	4
APPENDIX II: Error in Neon Polarizability Calculations Using a Commuting Potential . . . . .	8
II. PROPERTIES INVOLVING TWO-ELECTRON OPERATORS . . . . .	16
REFERENCES. . . . .	23

### PART II: LONG-RANGE INTERACTION OF HELIUM ATOMS; STUDY OF THREE AND FOUR ELECTRON CORRELATION EFFECTS

III. MANY-ELECTRON THEORY OF ATOMS . . . . .	25
INTRODUCTION . . . . .	25
ORBITAL PICTURE OF ATOMS . . . . .	25
MANY-ELECTRON THEORY . . . . .	29
IV. DISPERSION FORCES . . . . .	43
INTRODUCTION . . . . .	43
LONG-RANGE INTERACTION . . . . .	44

VARIED-PORIONS RESULT FOR HELIUM-HELIUM . . . . .	47
V. HELIUM-HELIUM CALCULATION . . . . .	55
COMPUTATIONAL DETAILS. . . . .	55
DISCUSSION . . . . .	68
REFERENCES. . . . .	75
VITA. . . . .	76



# LIST OF TABLES

Table	Page
I: Bagus-Gilbert Basis Set. . . . .	62
II: Hinze p-orbital Basis Set for $\varphi_{\alpha 10}$ . . . . .	62
III: Hinze Configuration Mixing Coefficients (renormalized) . . . . .	63
IV: Our Basis Set for $\varphi'_{\alpha 10}$ . . . . .	63
V: Inter-Atomic Configuration Mixing Coefficients . . . . .	64
VI: The $R^{-6}$ Coefficient Obtained at Stage I. . . . .	64
VII: The $R^{-6}$ Coefficient Obtained at Stage II . . . . .	65
VIII: The $R^{-6}$ Coefficient Obtained at Stage III. . . . .	65
IX: Wahl Basis Set for $\varphi'_{\alpha 10}$ . . . . .	66
X: Schaefer Basis Set for $\varphi'_{\alpha 10}$ . . . . .	66
XI: Schaefer and Wahl Mixing Coefficients. . . . .	67

## ABSTRACT

### Part I

The Varied-Portions Approach (VPA) of Sinanoğlu is used to bring the usual Hartree-Fock perturbation theories of second-order one-electron properties (polarizability, etc.) within the framework of a more general method. Theoretical difficulties inherent in a formal perturbation theory treatment of electron correlation corrections are avoided, and errors in various approximations to the Hartree-Fock potential can be systematically studied by the theory developed. A calculation is included which determines the size of such an error when electron correlation corrections to the polarizability of neon are calculated using a simple, non-local potential in place of the Hartree-Fock potential.

### Part II

The theoretical ideas in Part I are extended to treat the long-range interactions of atoms. Although the starting wavefunction is that of two Hartree-Fock atoms, the method does not define any zero-order Hamiltonian. Calculations are performed on the long-range  $R^{-6}$  interaction between two helium atoms, including three and four-electron correlation effects. Through pair excitations an upper limit of 1.3243 a.u. to the  $R^{-6}$  coefficient is found.

PART I: VARIED-PORIONS APPROACH  
TO SECOND-ORDER PROPERTIES

## I. PROPERTIES INVOLVING ONE-ELECTRON OPERATORS

Although the following appendices (Appendix I to be referred to as Paper I) contain the essential features of the Varied-Portions Approach (VPA) and its relation to perturbation theory, it should be emphasized here that the method is not itself a perturbation theory. It was derived from the energy variational principle to specifically avoid some theoretical difficulties inherent in obtaining, from a pure perturbation theory approach, electron correlation corrections to second-order, one-electron properties (polarizability, etc.).

In a perturbation theory one is required to replace the instantaneous electron repulsions, the  $r_{ij}^{-1}$  terms in the Hamiltonian, with some more tractable potential. Usually, as in the case of a Hartree-Fock perturbation theory, some sort of one-particle interaction with a potential averaged over the motions of all the other electrons is introduced. This gives one a solvable unperturbed system, but it also makes the potential non-local in character. It includes even the interaction of an electron with itself, the so-called "self-potential" terms. Consequently, the first order perturbation equation is transformed into a set of coupled, integro-differential equations. These, of course, can be solved to zero-order in electron correlation by either considerable computational effort, or some decoupling procedure.

But, if one then attempts to calculate first-order electron

correlation corrections, some difficulty can arise in using a decoupling procedure. In fact, the correlation correction terms have previously only been derived for one common form of uncoupled Hartree-Fock perturbation theory, the so-called Dalgarno Uncoupled Hartree-Fock Method, method (c) in reference (1) of Paper I. The reason, as Paper I points out, is that the common practice has been to use a double perturbation theory analysis and an interchange theorem to obtain electron correlation corrections. The advantage of such an approach is that it greatly simplifies the problem, because the correction terms can then be expressed without a need to know the wavefunction correct to first-order in electron correlation; only the orbitals already available from the uncoupled calculation are necessary. But, the disadvantage is that the Dalgarno method is the only one which can be subjected to this type of analysis. For, since it is the only one that retains the "self-potential" terms in the Hamiltonian, it is the only one that remains within perturbation theory. Other methods which leave these terms out no longer fall within the formalism because removing the self-potential terms puts each electron into a different unperturbed system (i.e., the Hartree-Fock potential would be different for each electron). For the other uncoupled methods one could calculate these same terms, and that is the practical choice made, but it is, from perturbation theory at least, not proper to do so. This may not seem a serious limitation until one realizes that empirically, in many instances, the decoupling procedures neglecting the self-potential terms yield very poor results. Consequently, one is

often faced with only being able to rigorously correct a result which may be a poor zero-order approximation.

It was to escape this dilemma of formal perturbation theory that the Varied-Portions Approach was utilized. We avoid the necessity of defining an unperturbed Hamiltonian at the outset. But, by taking the zero-order result of Hartree-Fock perturbation theory as a first approximation to the wavefunction in the energy variational procedure, the energy can be separated into a Hartree-Fock part, plus a remainder in the form of a variational expression. By proper partitioning of this remainder, all the decoupled, as well as the coupled, Hartree-Fock methods can be derived, with the advantage that now the electron correlation correction terms for all the methods are predicted. An added benefit of the Varied-Portions Approach is that errors introduced into the electron correlation corrections to a second-order property by using an approximation to the true Hartree-Fock potential can now be systematically studied. A calculation based on this aspect of the Varied-Portions Approach is carried out in Appendix II.

APPENDIX I

Reprint

VARIED-PORCTIONS APPROACH TO SECOND-ORDER PROPERTIES  
INVOLVING ONE-ELECTRON OPERATORS

B. R. Riemenschneider and N. R. Kestner  
Chem. Phys. Ltrs. 2 (1970) 381

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## APPENDIX II

This Appendix is a copy of an article submitted  
to Chemical Physics Letters entitled:

ERROR IN NEON POLARIZABILITY CALCULATIONS  
USING A COMMUTING POTENTIAL

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## II. PROPERTIES INVOLVING TWO-ELECTRON OPERATORS

As demonstrated in the previous sections, the Varied-Portions Approach offers significant theoretical advantages over pure perturbation theory in dealing with properties represented by one-electron operators. But a point of interest is whether the same advantage accrues in the case of properties involving two-electron operators, such as the multipole interaction of two atoms.

It is already well known that this problem in inter-molecular forces, at distances where the multipole expansion is valid (no overlap) can be transformed from one two-center problem to two one-center problems. This is possible because the second-order energy can be written as the integral over imaginary frequencies of the dynamic polarizabilities of the separate atoms, A and B. For instance, for the dipole-dipole interaction one would have

$$E_{AB}^{(2)} = - \frac{3}{\pi R^6} \int_0^{\infty} \alpha_A(i\omega) \alpha_B(i\omega) d\omega \quad . \quad (1)$$

The derivation of equation (1) is well documented in many references [1] [2] and will not be repeated here. But, the point to note is that at each frequency  $\omega$  the problem becomes that of calculating the polarizability of each center separately. This is usually done by a time-dependent Hartree-Fock perturbation theory, and was the method used by Broussard and Kestner [3] to obtain the polarizabilities of

neon. It is commonly referred to as the one-center method, for obvious reasons.

Not a small part of the advantage of such an approach is that one can again escape the necessity of having to know the intra-atomic correlated wavefunction when calculating electron correlation corrections to  $\alpha_A(i\omega)$ . As demonstrated by D. F. Tuan [4], and already referred to in Paper I, this is made possible by the application of Brillouin's theorem and an interchange theorem. Brillouin's theorem insures that the only part of the second-order wavefunction that contributes to the second-order energy is actually a product of two lower-order effects, two first-order perturbed functions already available from the lower-order calculation. The interchange theorem establishes the equivalence of matrix elements of two different perturbations [5] [6], the external field and the error in the zero-order Hamiltonian. Thus, one can calculate the electron correlation corrections to the second-order energy using just that part of the second-order wavefunction which does not contain intra-atomic correlation orbitals [4]. This is an enormous simplification of the problem, and the Varied-Portions Approach was able to extend it to methods where it previously was not possible.

Recently, however, it has been suggested that perhaps an interchange theorem could be used to avoid intra-atomic correlated wavefunctions even in a two-center formulation [2]. The advantage of using a two-center method is that it is a stationary-state formulation of the problem. Thus, instead of having to compute the

polarizabilities at many different imaginary frequencies in order to carry out the numerical integration of equation (1), one only has one static perturbation equation to solve for the second-order energy.

In a double perturbation formalism Dalgarno [2] has shown that for real wavefunctions the second-order interaction energy can be expanded

$$E_{AB}^{(2)} = E_{AB}^{(0,2)} + E_{AB}^{(1,2)} + \dots \quad , \quad (2)$$

where 
$$E_{AB}^{(0,2)} = \langle \psi_A^{00} \psi_B^{00} | U | \Psi^{(0,1)} \rangle \quad , \quad (3)$$

and 
$$E_{AB}^{(1,2)} = 2 \langle \Psi^{(1,0)} | U | \Psi^{(0,1)} \rangle + \langle \Psi^{(0,1)} | V | \Psi^{(0,1)} \rangle \quad . \quad (4)$$

The first superscript refers to the order in intra-atomic electron correlation and the second to inter-atomic electron correlation.  $V = v_A(\vec{r}) + v_B(\vec{\rho})$  are the intra-atomic electron interactions as a function of the electronic coordinates  $\vec{r}$  and  $\vec{\rho}$  on centers A and B; and U is the inter-atomic electron interaction, a function of R, the distance between centers at large separations. In this discussion we shall consider only the dipole-dipole term in the multipole interaction,  $U(R^{-3})$ . If  $\psi_A^{00}$  and  $\psi_B^{00}$  are identified as the Hartree-Fock approximations to the eigenfunctions of the separated systems, then  $E_{AB}^{(0,2)}$  is identical to the uncoupled Hartree-Fock value obtained from the single-center method,  $E_{AB}^{(2)}$  of equation (1). The  $\Psi^{(1,0)}$  are wavefunctions including intra-atomic correlation to first-order. These

are the wavefunctions one can avoid in the one-center method. By using an interchange theorem Dalgarno has shown that [6]

$$\langle \Psi^{(0,2)} | V | \psi_A^{00} \psi_B^{00} \rangle = \langle \Psi^{(1,0)} | U | \Psi^{(0,1)} \rangle \quad (5)$$

$$\text{Thus,} \quad E_{AB}^{(1,2)} = 2 \langle \Psi^{(0,2)} | V | \psi_A^{00} \psi_B^{00} \rangle + \langle \Psi^{(0,1)} | V | \Psi^{(0,1)} \rangle \quad , \quad (6)$$

and the expression no longer contains intra-correlated wavefunctions. However, unless the contributing parts of  $\Psi^{(0,2)}$  are products of lower order effects, this procedure is of dubious advantage.

Considering the relevant perturbation equations, we operator analyze the relevant wavefunctions in order to separate the various effects into the terms of the Varied-Portions Approach and Many-Electron Theory of Sinanoğlu. The necessary perturbation equations are

$$(H^0 - E^0) \Psi^{(0,2)} + U \Psi^{(0,1)} - E^{(0,2)} \Psi^{(0,0)} = 0 \quad (7)$$

$$(H^0 - E^0) \Psi^{(0,1)} + U \Psi^{(0,0)} = 0 \quad .$$

$$\text{Writing} \quad H^0 - E^0 = \sum_{i=1}^{N_A} \tilde{e}_i + \sum_{\rho=N_A+1}^{N_B} \tilde{e}_\rho \equiv \tilde{L}_0 \quad , \quad (8)$$

$$\text{and} \quad U(R) = \sum_{i,v} w_{i,v} \quad , \quad (9)$$

(in our case we have  $w_{i,v} \propto Z_i Z_v R^{-3}$  where the  $Z_i$  are the z-coordinates

of electrons  $i$  and  $\nu$ ; Arabic indices on center A and Greek indices of center B) the operator solution to the first-order equation [7] [8] is

$$\Psi^{(0,1)} = \tilde{L}_O^{-1} \sum_{i,\nu} w_{i\nu} \Psi^{(0,0)} \quad , \quad (10)$$

where  $\Psi^{(0,0)} = \psi_A^{00} \psi_B^{00}$ . The  $\psi_A^{00}$  and  $\psi_B^{00}$  are the previously mentioned Hartree-Fock eigenfunctions given by

$$\psi_A^{00} = \mathcal{A}(\varphi_1(\vec{x}_1) \varphi_2(\vec{x}_2) \dots \varphi_{N_A}(\vec{x}_{N_A})) = \mathcal{A}(\varphi_1(1) \varphi_2(2) \dots \varphi_{N_A}(N_A)) \quad (11)$$

$$\psi_B^{00} = \mathcal{B}(\varphi_{N_A+1}(\vec{x}_{N_A+1}) \dots \varphi_{N_B}(\vec{x}_{N_B})) = \mathcal{B}(\varphi_{N_A+1}(N_A+1) \dots \varphi_{N_B}(N_B)), \quad (12)$$

where  $\vec{x}_i$  stands for both the spatial and spin coordinates of electron  $i$ . For compactness we also introduce the following notation:

$$\Gamma(A;i) = (\varphi_1(1) \dots \varphi_{i-1}(i-1) \varphi_{i+1}(i+1) \dots \varphi_{N_A}(N_A)) \quad (13)$$

$$\Gamma(B;\nu) = (\varphi_{N_A+1}(N_A+1) \dots \varphi_{\nu-1}(\nu-1) \varphi_{\nu+1}(\nu+1) \dots \varphi_{N_B}(N_B)). \quad (14)$$

We then write  $\Psi^{(0,1)}$  as

$$\begin{aligned} \Psi^{(0,1)} &= - \tilde{L}_O^{-1} \sum_{i,\nu} w_{i\nu} \psi_A^{00} \psi_B^{00} \\ &= - \mathcal{A} \mathcal{B} \{ \tilde{L}_O^{-1} \sum_{i,\nu} \Gamma(A;i) \Gamma(B;\nu) w_{i\nu} \varphi_i(i) \varphi_\nu(\nu) \} \quad . \quad (15) \end{aligned}$$

Reducing this operator equation [9] gives

$$\begin{aligned}\Psi^{(0,1)} &= \alpha^A \alpha^B \left\{ \sum_{i,v} \Gamma(A;i) \Gamma(B;v) \frac{1}{\tilde{e}_i + \tilde{e}_v} w_{iv} \varphi_i(i) \varphi_v(v) \right\} \\ &= - \alpha^A \alpha^B \left\{ \sum_{i,v} \Gamma(A;i) \Gamma(B;v) u_{iv}^{(1)} \right\} \quad .\end{aligned}\quad (16)$$

The  $u_{iv}^{(1)}$  must then satisfy the two-electron equation

$$(\tilde{e}_i + \tilde{e}_v) u_{iv}^{(1)} - w_{iv} \varphi_i(i) \varphi_v(v) = 0. \quad (17)$$

Thus, one sees that  $\Psi^{(0,1)}$  is essentially a two-electron effect between two centers. The effect is represented by the inter-atomic pair function  $u_{iv}^{(1)}$ . For the dipole-dipole case and spherically symmetric atoms this could be considered as one p-excitation on each center resulting from the inter-atomic interaction  $U(R^{-3})$ .

Using the same procedure on  $\Psi^{(0,2)}$  we find

$$\begin{aligned}\Psi^{(0,2)} &= - \tilde{L}_O^{-1} \{ U \Psi^{(0,1)} \} \\ &= \tilde{L}_O^{-1} \sum_{j,\rho} w_{j\rho} \alpha^A \alpha^B \{ \tilde{L}_O^{-1} \sum_{i,v} \Gamma(A;i) \Gamma(B;v) w_{iv} \varphi_i(i) \varphi_v(v) \}. \quad (18)\end{aligned}$$

Depending on the values of the four indices, this leads to three different terms

$$\Psi_{IV}^{(0,2)} = \alpha^A \alpha^B \left\{ \sum_{\substack{i,v \\ j,\rho}} \binom{i \neq j}{v \neq \rho} \Gamma(A;i) \Gamma(B;\rho) u_{iv}^{(1)} u_{j\rho}^{(1)} \right\} \quad (19)$$



$$\Psi_{III}^{(0,2)} = \alpha^A \alpha^B \frac{1}{\sqrt{2}} \left\{ \sum_{i,\rho,\nu} (\rho \neq \nu) \Gamma(A;i) \Gamma(B;\rho\nu) u_{i\rho\nu}^{(2)} \right\} \quad (20)$$

$$\Psi_{II}^{(0,2)} = \alpha^A \alpha^B \left\{ \sum_{i,\nu} \Gamma(A;i) \Gamma(B;\nu) u_{i\nu}^{(2)} \right\} \quad (21)$$

The factor  $2^{-1/2}$  comes from the antisymmetry requirement that  $u_{i\rho\nu}^{(2)}$  be antisymmetric on one center only. Because of the neglect of overlap, antisymmetry between centers is not required [10].

The second-order wavefunction, then, has three parts: a true second-order correlated part,  $u_{i\nu}^{(2)}$ ; a product of two lower-order parts,  $u_{i\nu}^{(1)} u_{j\rho}^{(1)}$ ; and a second-order part,  $u_{ij\rho}^{(2)}$ . The first two are two-electron effects while the last is a three-electron effect. It is this wavefunction that one would choose to use in a Varied-Portions Approach. Following earlier work contained in Paper I, one can put the wavefunction  $\Psi = \Psi^{(0,0)} + \Psi^{(0,1)} + \Psi^{(0,2)}$  into  $E < \frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle}$  and derive a variational expression from which the uncoupled Hartree-Fock perturbation equations for two-electron operators emerge as special cases. But, it is immediately evident that, in the energy matrix elements for  $E_{AB}^{(1,2)}$ , only the  $u_{i\nu}^{(2)}$  and  $u_{i\nu}^{(1)} u_{j\rho}^{(1)}$  contributions from  $\Psi^{(0,2)}$  vanish. The three-electron effect does not vanish, nor has a way been found to express it as a lower-order effect.

In conclusion, then, the approach used in the one-electron operator case does not bear fruit in the two-electron operator case. One cannot escape the requirement of needing to know the intra-atomic correlated wavefunctions, as long as one has formulated the problem as a stationary-state two-center problem.

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PART II: LONG-RANGE INTERACTION OF HELIUM ATOMS;  
STUDY OF THREE AND FOUR ELECTRON  
CORRELATION EFFECTS

### III. MANY-ELECTRON THEORY OF ATOMS

#### INTRODUCTION

The calculations done in this chapter are based on the Many-Electron Theory of Sinanoğlu. It is covered in great detail in several excellent articles and reviews [1]-[5], and little or nothing could be added to the discussions contained therein by an intricate discussion here. Nevertheless, in order to understand the significance of the effects and approximations used in this calculation, it would be helpful to cover the salient points in the philosophy of the Many-Electron Theory before deriving the equations appropriate to the long-range inter-atomic forces considered here. This discussion will be limited to closed shell atoms, since the extension to non-closed shells involves features of little use to the calculations later performed.

#### ORBITAL PICTURE OF ATOMS

By introducing atomic units\* one may write the exact Hamiltonian of an N-electron atomic system as

$$H = -\frac{1}{2} \sum_{i=1}^N \nabla_i^2 - \sum_{i=1}^N \frac{Z}{r_i} + \sum_{i<j} \frac{1}{r_{ij}}, \quad (1)$$

---

\*  $\hbar = m_e = e = 1$ ; the unit of energy is the Hartree = 27.21 ev.; the unit of distance is the Bohr = .52917 Å;  $e$  = charge on the electron;  $m_e$  = mass of electron.

where  $Z$  denotes the nuclear charge. Any system can then be described completely by the Schroedinger equation

$$H\Psi_{\text{EXACT}} = E\Psi_{\text{EXACT}} \quad (2)$$

-- if one could solve it. This, for atoms of course, is only possible for the hydrogen atom, where a nice tangible orbital picture emerges. It is satisfying because there is a "place" to "put" each electron, and each is thought of as having some sort of physical reality. This orbital picture is quite appealing, and even when carried over to larger systems in just a qualitative sense it has been responsible for elucidating most that is known about chemical structure. So, the fundamentally abstract nature of quantum theory and its wavefunction notwithstanding, this orbital picture clearly possesses some fundamental validity.

To maintain the picture and yet quantitatively treat larger systems by Schroedinger's equation we seek solutions that allow one to write the wavefunction for an  $N$ -electron system as some sort of product of one-electron functions

$$\Psi = \varphi_1(\vec{x}_1)\varphi_2(\vec{x}_2)\dots\varphi_N(\vec{x}_N) \quad , \quad (3)$$

where  $\vec{x}_i$  stands for both spatial and spin coordinates of electron  $i$ . The  $\varphi_i(\vec{x}_i)$  are thus spinorbitals. The exclusion principle, of course,

requires this be antisymmetrized,\*

$$\Psi^0 = \alpha(\varphi_1(\vec{x}_1)\varphi_2(\vec{x}_2)\dots\varphi_N(\vec{x}_N)) \quad , \quad (4)$$

but the important thing is that this form implies independence of the one-electron functions, or orbitals  $\varphi_i$ . Such a solution is only possible if the exact Hamiltonian is decomposable into a sum of one-electron terms

$$H = h_1 + h_2 + \dots + h_N \quad . \quad (5)$$

In general one is unable to do this exactly, so an approximation is made. For this discussion we assume it is the common Hartree-Fock one. It gives the best one-electron orbitals to use in writing equation (4) by letting each electron move in a potential averaged over the motions of the other electrons in the system. Each orbital is found to satisfy an effective Schroedinger equation

$$h_i^{\text{eff}} \varphi_i^0 = \epsilon_i^0 \varphi_i^0 \quad , \quad (6)$$

where,

$$h_i^{\text{eff}} = h_i^0 + V_i^{\text{HF}} \quad , \quad (7a)$$

---

\*In non-closed shell systems the wavefunction is complicated by the need to use several terms of this general form, but only closed shell systems are considered here.

$$h_i^0 = -\frac{1}{2} \nabla_i^2 - \frac{Z}{r_i} \quad , \quad (7b)$$

$\epsilon_i^0$  are the orbital energies given by

$$\begin{aligned} \epsilon_i^0 = & \langle \varphi_i^0(i) | h_i^{\text{eff}} | \varphi_i^0(i) \rangle + \sum_{j \neq i} \{ \langle \varphi_i^0(i) \varphi_j^0(j) | \frac{1}{r_{ij}} | \varphi_i^0(i) \varphi_j^0(j) \rangle \\ & - \langle \varphi_i^0(i) \varphi_j^0(j) | \frac{1}{r_{ij}} | \varphi_j^0(i) \varphi_i^0(j) \rangle \} \quad , \end{aligned} \quad (8)$$

and  $V_i^{\text{HF}}$  is the familiar Hartree-Fock potential. This defines a zero-order system by the Hamiltonian

$$H^0 = \sum_i h_i^{\text{eff}} = \sum_i (h_i^0 + V_i) \quad , \quad (9)$$

where the Hartree-Fock wavefunction is the antisymmetrized product of spinorbitals  $\varphi_i^0$  from equation (6). The difference between the exact Hamiltonian and  $H^0$ ,

$$H^1 = \sum_{i < j} \frac{1}{r_{ij}} - \sum_i V_i^{\text{HF}} \quad , \quad (10)$$

is then treated as the error in the  $H^0$  approximation (in the language of perturbation theory  $H^0$  is the unperturbed system). The Hartree-Fock energy is then given by

$$E_{\text{HF}} = \langle \Psi^0 | H | \Psi^0 \rangle \quad . \quad (11)$$

The picture given by the Hartree-Fock approach has had a great deal of success in accounting for much qualitative chemical and spectroscopic behavior. Nevertheless, calculations of the energy often yield large discrepancies when compared with experiment. In certain cases the formation of stable molecules may not even be predicted [1]. Obviously, then, a theory that only accounts for the average interaction potentials of the electrons can be in serious error.

#### MANY-ELECTRON THEORY

Objectives.--The previous section emphasizes that results of Hartree-Fock theory, while often quantitatively in error, still seem to bear out the fundamental correctness of the orbital picture. Nevertheless, the large discrepancies in the Hartree-Fock approach indicate that deviations from the average potential must be considered in accurate calculations. The difference between the actual, non-relativistic energy and the Hartree-Fock energy is due to the difference between the exact interactions and the averaged interactions. That is, one is really dealing with correlated motion of the electrons, and the error in the energy is called the correlation energy. In view of this, the Many-Electron Theory confronts the N-electron problem with the following objectives [1] [2]:

1. recognize the semi-empirical success of the orbital picture
2. systematically consider the various contributions to electron correlation



3. develop a method which does not become rapidly more difficult as the number of electrons increases
4. maintain a physical picture in the wavefunction.

Relation to Perturbation Theory.--Although the Many-Electron Theory approach to the long-range interactions of helium in this dissertation is actually handled from the Varied-Portions Approach viewpoint, when discussing the ideas in general it is more instructive to relate it to perturbation theory. It is somewhat easier, then, to identify the various effects as they enter the theory. But, in the actual calculation this is not necessary, in fact not even desirable, and this will be pointed out at the proper time.

The eigenvalue problem

$$H\Psi = E\Psi \quad (12)$$

is equivalent to finding a  $\Psi$  such that

$$\delta\{\langle\Psi|H|\Psi\rangle / \langle\Psi|\Psi\rangle\} = 0 \quad , \quad (13)$$

where  $\delta$  stands for all possible variations in the wavefunction  $\Psi$ .

Furthermore, if  $\Psi$  is the lowest state of an irreducible representation, then for any trial function  $\tilde{\Psi}$  we have an upper limit [6] to the energy given by

$$E < \frac{\langle\tilde{\Psi}|H|\tilde{\Psi}\rangle}{\langle\tilde{\Psi}|\tilde{\Psi}\rangle} \quad . \quad (14)$$

If one expands as follows

$$E = E^0 + E^1 + \dots \quad (15a)$$

$$H = H^0 + H^1 \quad (15b)$$

$$\Psi = \Psi^0 + \tilde{\chi} \quad (15c)$$

where  $H^0 \Psi^0 = E^0 \Psi^0$  , (15d)

one gets

$$E < \frac{\langle \Psi^0 + \tilde{\chi} | H^0 + H^1 | \Psi^0 + \tilde{\chi} \rangle}{\langle \Psi^0 + \tilde{\chi} | \Psi^0 + \tilde{\chi} \rangle} . \quad (16)$$

Assuming  $\langle \Psi^0 | \Psi^0 \rangle = 1$  and clearing  $E^0 + E^1$  from the numerator, a bit of algebraic manipulation will give

$$E < E^1 + E^0 + E_R(\chi) , \quad (17)$$

where 
$$E_R(\chi) = \frac{2\langle \Psi^0 | q | \tilde{\chi} \rangle + \langle \tilde{\chi} | e | \tilde{\chi} \rangle + \langle \tilde{\chi} | q | \tilde{\chi} \rangle}{1 + 2\langle \Psi^0 | \tilde{\chi} \rangle + \langle \tilde{\chi} | \tilde{\chi} \rangle} , \quad (18)$$

with  $q = H^1 - E^1$  ,

and  $e = H^0 - E^0$ .

Since in many cases it is not possible to make the entire  $E_R(\tilde{\chi})$  stationary, one can minimize just a large portion of it. A major part that can be made stationary is

$$2\langle \Psi^0 | q | \tilde{\chi} \rangle + \langle \tilde{\chi} | e | \tilde{\chi} \rangle \quad , \quad (19)$$

but this just yields the variational expression one would find equivalent to solving the first-order perturbation eigenvalue problem. So, at the minimum,  $\tilde{\chi}$  is just the  $\Psi^1$  found from ordinary Raleigh-Schroedinger perturbation theory. The extension to higher orders in perturbation theory has been discussed by Sinanoğlu [7].

Note that going from equation (14) to equation (16) corresponds to adding and subtracting a potential  $V$  to the total Hamiltonian and re-writing the numerator. In any calculation the result from equation (14) would be equivalent to that from equation (16); the terms when expanding the numerator may appear in different places, but there is no fundamental difference in the two starting points. They are both a variational approach, and the Varied-Portions Approach would suggest that the numerator of equation (18) be split-up and a large part, such as equation (19), be minimized. Computationally, it is easier to apply the Varied-Portions Approach to equation (14), but physically it is easier to see the effects in the Many-Electron Theory by starting from equation (16) as we have done here.

If the potential  $V$  is chosen as the Hartree-Fock potential,  $V^{HF}$ , equation (17) becomes

$$E < E_{\text{HF}} + E_R(\tilde{\chi}) \quad . \quad (20)$$

For closed shell systems the Many-Electron Theory usually starts from this equation. It is equivalent to recognizing the Hartree-Fock wavefunction as the best first estimate for any many-electron system. Correlation is then introduced in  $\tilde{\chi}$  in such a way that the major effects can be rigorously isolated and reasonable approximations made based on chemical or physical evidence. Hopefully, the N-electron problem will reduce to a series of few-electron problems.

Fluctuation Potential.--In obtaining equation (20) one takes the exact Hamiltonian

$$H = \sum_i h_i^0 + \sum_{i<j} g_{ij} \quad (21)$$

and separates it into an independent-electron part (the unperturbed system)

$$H^0 = \sum_i (h_i^0 + v_i^{\text{HF}}) \quad , \quad (22)$$

and a residual potential part

$$H^1 = \sum_{i<j} g_{ij} - \sum_i v_i^{\text{HF}} \quad (23)$$

so that  $H = H^0 + H^1$  and  $E_{\text{HF}} = E^0 + E^1$  . One then has the following relations [1]:

$$H - E_{\text{HF}} = H^0 - E^0 + H^1 - E^1 \quad (24)$$

$$= \sum_i e_i + \sum_{i<j} m_{ij} \quad (25)$$

$$e_i = h_i^0 + v_i^{\text{HF}} - \epsilon_i^0 \quad (26)$$

$$\sum_{i<j} m_{ij} = H^1 - E^1 \quad (27)$$

The quantity  $m_{ij}$  represents the instantaneous deviation of the potential between electrons  $i$  and  $j$  from the average Hartree-Fock value and is called the fluctuation potential [1]. Substituting this into  $E_R(\tilde{\chi})$  one gets

$$E_R(\tilde{\chi}) = \frac{2\langle \Psi^0 | \sum_{i<j} m_{ij} | \tilde{\chi} \rangle + \langle \tilde{\chi} | \sum_i e_i + \sum_{i<j} m_{ij} | \tilde{\chi} \rangle}{1 + \langle \tilde{\chi} | \tilde{\chi} \rangle} \quad (28)$$

This form suggests that one might consider most of the correlation to be caused by "collisions" between pairs of electrons.

Many-Electron Wavefunction.---Any exact wavefunction can be written

$$\Psi = \Psi^0 + \chi \quad (29)$$

(with proper normalization) where  $\Psi^0$  is the closed shell (or non-closed,

but we only consider the former here) Hartree-Fock wavefunction and  $\chi$  is everything left over. In particular one requires  $\langle \Psi^0 | \chi \rangle = 0$  to completely separate the two portions. The  $\Psi^0$ , then, puts in the average repulsions of the electrons, and  $\chi$  brings in the residual electron-electron effects due to the fluctuation potentials [2]. It corrects for the "collisions" among progressively larger numbers of electrons in the Hartree-Fock "sea". One says that such a collision occurs if two electrons come within range of their  $m_{ij}$ .

Hence, for a closed shell system the Many-Electron Theory exact correlation wavefunction is [1]

$$\chi = \sum_i \{f_i\} + \sum_{i < j} \{U_{ij}\} + \sum_{ijk} \{U_{ijk}\} + \dots \quad , \quad (30)$$

where

$$\{f_i\} = \alpha \{\Gamma(A; i) \hat{f}_i\}$$

$$\{U_{ij}\} = \frac{\alpha}{\sqrt{2!}} \{\Gamma(A; ij) \hat{u}'_{ij}\}$$

etc. (see equation (II:13) for notation), and each term takes into account correlation among larger and larger clusters of electrons. Each correlation function is orthogonal to all spinorbitals occupied in  $\Psi^0$  and this is denoted by the carat. This orbital orthogonality involves two effects for a given correlation function:

- (a) orthogonality to its own orbitals
- (b) orthogonality to all others occupied in  $\Psi^0$ .

Effect (a) comes about because correlations involving fewer electrons

have been separated out in some other term; effect (b) means that when electrons  $i$  and  $j$  are correlating with one another they are prevented by the Pauli principle from going into orbitals  $k \neq i, j$  of  $\Psi^0$  already occupied. For this reason (b) is referred to as the exclusion effect [2].

The wavefunction in equation (30) is still not detailed enough because it fails to distinguish between two types of electron correlation. For instance, a four-electron term  $\hat{u}'_{ijkl}$  could mean a true four-body collision, or it could mean two two-body collisions occurring at the same "time" in different parts of the sea. These simultaneous collisions are only implicit in equation (30), but in analogy to statistical mechanics one could distinguish linked and unlinked clusters in the wavefunction. In doing this we would write, for instance,

$$\hat{u}'_{ij} = \mathcal{O}_{ij} \{ \hat{f}_i \hat{f}_j + \hat{u}_{ij} \} \quad (31a)$$

$$\hat{u}'_{ijk} = \mathcal{O}_{ijk} \{ \hat{f}_i \hat{f}_j \hat{f}_k + \hat{f}_i \frac{\hat{u}_{jk}}{\sqrt{2}} + \hat{f}_j \frac{\hat{u}_{ik}}{\sqrt{2}} + \hat{f}_k \frac{\hat{u}_{ij}}{\sqrt{2}} + \hat{u}_{ijk} \} \quad , \quad (31b)$$

where each  $\hat{u}'_{ij\dots N}$  would consist of all possible antisymmetrized products of the preceding fewer-electron terms not containing any indices in common ( $\mathcal{O}_{ij\dots N}$  is the antisymmetrizer for the electrons denoted by its subscripts), and a new linked-cluster term  $\hat{u}_{ij\dots N}$  without the prime. The exact  $\chi$ , then, contains

- (i) the effect of correlation of orbitals,  $\hat{f}_i$
- (ii) two-electron correlations,  $\hat{u}_{ij}$
- (iii) many-electron correlations, the other  $\hat{u}_{ij\dots N}$
- (iv) unlinked clusters of these terms.

If this exact  $\chi$  is used to determine  $E_R(\chi)$  the total energy would be

$$E = E_{HF} + \sum_{i < j} \langle \alpha_{ij}(\varphi_i \varphi_j) | g_{ij} | \hat{u}_{ij} \rangle \quad . \quad (32)$$

However, this applies only to the exact  $E$  and  $\chi$ . It is not a useful theory yet because the many-electron terms are not necessarily decoupled and may very well depend upon one another. The theory at this point is purely a formal one, no method has been defined for calculating these effects in some simple way.

To arrive at the simplest realistic theory, one must examine the magnitudes of

- (i) the  $\hat{f}_i$
- (ii) the pair correlations  $\hat{u}_{ij}$
- (iii)  $n$ -electron correlations ( $n > 2$ ) in  $\chi$ .

Workable Theory.--If, as the form of equation (28) suggests, most of the correlation is caused by pair interactions, we should expect correlations involving more than two electrons to be small. This conclusion is indeed supported by considering the effect of antisymmetry on the relative positions of the electrons and the range of the  $m_{ij}$ . The relative distribution of electrons in  $\psi^0$  depends on



the molecular geometry and the Fermi holes between like-spin orbitals. Considering any three electrons in the Hartree-Fock sea which might come near each other, at least two of these will have the same spin and the exclusion principle will tend to keep them apart. Furthermore, the  $m_{ij}$  are not long-range like the  $r_{ij}^{-1}$  interaction; they usually die out before reaching the third electron [2]. These arguments are confirmed by Hartree-Fock plus Configuration-Interaction calculations on the Beryllium atom and Lithium-hydride molecule [8] [9]. Triply excited configurations (corresponding to three-electron correlations) were found to be insignificant. Also, what appeared to be four-electron effects were later [2] shown to be just products of two two-electron effects.

The  $\hat{f}_i$  represent the effect of correlation on the orbitals; that is, the change in the electron distribution caused by correlation. Their effect on the energy has been examined in detail [1] [4] and it was found to be unimportant. This merely confirms the earlier premise that the Hartree-Fock  $\Psi^0$  wavefunction provides a valid starting point to begin constructing a theory accounting for electron correlation.

Therefore, the pair correlations and their unlinked clusters become the working wavefunction from which to develop equation (28) into a useful form. The correlation wavefunction  $\chi$  for a closed shell, N-electron system is then taken as [3]

$$\chi'_S = \chi_S + \chi_{SS} + \chi_{SSS} + \dots, \quad (33)$$

where 
$$\chi_s = \alpha \left\{ \frac{1}{\sqrt{2!}} \sum_{i < j} \Gamma(A; ij) \hat{u}_{ij} \right\} \equiv \sum_{i < j} \{ \hat{u}_{ij} \} \quad (34)$$

$$\chi_{ss} = \alpha \frac{1}{2!} \left\{ \sum_{\substack{i < j \\ i, j \neq k, l}} \sum_{k < l} \Gamma(A; ijkl) \hat{u}_{ij} \hat{u}_{kl} \right\} \equiv \sum_{\substack{i < j \\ ij \neq kl}} \sum_{k < l} \{ \hat{u}_{ij} \hat{u}_{kl} \} \quad (35)$$

etc.,

and the prime on  $\chi'_s$  indicates the inclusion of unlinked cluster terms.

It is important to note the following advantages of this form:

- (i) It is not an infinite series (contrary to Configuration-Interaction methods) if the system has a finite number of electrons.
- (ii) It is in a very detailed form so that each term can be examined and systematic approximations made to the  $\hat{u}_{ij}$ 's.
- (iii) The  $\hat{u}_{ij}$  are in closed form.

If we now substitute  $\chi'_s$  into equation (28) we get

$$E_R(\chi'_s) = \frac{2 \langle \Psi^0 | \sum_{i < j} m_{ij} | \chi'_s \rangle + \langle \chi'_s | \sum_i e_i + \sum_{i < j} m_{ij} | \chi'_s \rangle}{1 + \langle \chi'_s | \chi'_s \rangle} \quad (36)$$

The matrix elements in the numerator reduce to:

$$\langle \Psi^0 | \sum_{i < j} m_{ij} | \chi'_s \rangle = \sum_{i < j} \langle a_{ij}(\varphi_i \varphi_j) | m_{ij} | \hat{u}_{ij} \rangle \quad (37)$$

$$\begin{aligned}
\langle \chi'_s | \sum_i e_i + \sum_{i<j} m_{ij} | \chi'_s \rangle &= \sum_{i<j} \langle \hat{u}_{ij} | e_i + e_j + m_{ij} | \hat{u}_{ij} \rangle \\
&+ \sqrt{3}! \sum_{i<j<k} \langle \varphi_i \hat{u}_{kj} | m_{ji} | \mathcal{Q}_{ijk}(\hat{u}_{ik} \varphi_j) \rangle .
\end{aligned} \tag{38}$$

This gives the final usable form of equation (28) in the Many-Electron Theory as

$$E_R(\chi'_s) = \sum_{i<j} \frac{\epsilon_{ij} D_{ij}}{D'} + \frac{\mathcal{R}}{D'} . \tag{39}$$

The quantities in this expression are given by

$$\epsilon_{ij} = 2 \langle \mathcal{Q}_{ij}(\varphi_i \varphi_j) | m_{ij} | \hat{u}_{ij} \rangle + \langle \hat{u}_{ij} | e_i + e_j + m_{ij} | \hat{u}_{ij} \rangle \tag{40}$$

$$D' = 1 + \langle \chi_s | \chi_s \rangle + \langle \chi_{ss} | \chi_{ss} \rangle + \dots \tag{41}$$

$$\mathcal{R} = \sqrt{3}! \sum_{i<j<k} \langle \varphi_i \hat{u}_{kj} | m_{ji} | \mathcal{Q}_{ijk}(\hat{u}_{ik} \varphi_j) \rangle . \tag{42}$$

The  $D_{ij}$  is  $D'$  with all terms involving  $\hat{u}_{ij}$  left out.

It has been demonstrated [3] that

$$\frac{D_{ij}}{D'} \cong \frac{1}{D} , \tag{43}$$

where

$$D = 1 + \langle \hat{u}_{ij} | \hat{u}_{ij} \rangle . \tag{44}$$



$$\sqrt{3}! \langle \varphi_i u_{kj} | m_{ji} | a_{ijk} (u_{ik} \varphi_j) \rangle = \begin{array}{c} i \quad k \\ \circ \text{---} \circ \\ \quad \quad \quad \diagdown \\ \quad \quad \quad \circ \\ \quad \quad \quad j \end{array} \quad (49)$$

The solid line represents a pair correlation in the wavefunction and the dotted line corresponds to the operation of a fluctuation potential  $m_{ij}$ . The  $\mathcal{R}$  contains the sum of many ( $n > 3$ )-electron correlations and the first terms would be of the type

$$\begin{array}{c} l \quad k \\ \circ \text{---} \circ \\ \quad \quad \quad \diagdown \\ \quad \quad \quad \circ \\ \quad \quad \quad j \\ i \end{array} \quad (50)$$

These are expected to be small for the same reason that we earlier considered three-electron correlations to be small. The quadrangles represent four-electron correlations which, in view of the exclusion principle, are even less likely to occur than those between three electrons.

This discussion so far has been limited to single atoms. In the next chapter extension will be made to dispersion forces between atoms. However, the atomic approach was simpler, and quite adequate to illustrate the important points of the theory.

#### IV. DISPERSION FORCES

##### INTRODUCTION

The essential features of a workable Many-Electron Theory accounting for electron correlation were developed in the previous chapter with that discussion dealing only with closed shell atoms. It now remains to extend the theory to the specific case treated here, that of the interaction of two closed shell atoms at inter-nuclear distances where overlap is essentially zero. These dispersion "forces", as they are named, turn out to be a purely quantum mechanical effect. Neutral closed shell atoms are spherically symmetric and therefore possess neither a net charge nor any electric moment. If they are considered as classical static systems, classical ideas provide no mechanism to even predict an interaction. However, there is ample physical evidence to indicate that some interaction does take place, the behavior of real gases being a prime example.

Quantum theory with its "zero-point motion" provides the only source of these interactions. It says that electrons according to the uncertainty principle must be in constant motion. These motions create instantaneous deviations from the homogeneous spherical charge distribution and thus produce momentary electric moments. When an electric moment is produced in a nearby atom, either by induction or by the motion of its own electrons, the moments of the two atoms interact in such a way as to lower the energy of the system

and lead to an attraction. The predominant effect is an attraction between dipoles behaving as  $R^{-6}$ . In interacting through these electric moments the motions of the electrons on one atom become correlated with the motions of the electrons on the other. Consequently, one can calculate these dispersion forces\* by treating them as a two-center electron correlation problem.

#### LONG-RANGE INTERACTION

Multipole Expansion.--We now consider two closed shell atoms far enough apart so that there is no overlap of their electronic charges. The Hamiltonian would be given by

$$H = H_A + H_B + U(R) \quad , \quad (1)$$

where  $H_A$  and  $H_B$  are the atomic Hamiltonians of the isolated atoms, and  $U(R)$  is the long-range interaction of the two centers A and B. It is well known [10] that this interaction can be expressed as a multipole expansion

$$U(R) = \sum_{\ell=0}^{\infty} \sum_{L=0}^{\infty} \frac{W_{\ell L}}{R^{\ell+L+1}} \quad (2)$$

where the  $\ell L$ -term arises from the interaction between a  $2^{\ell}$ -pole on one center with a  $2^L$ -pole on the other. These interactions involve individual pairs of electrons and can be written in a form due to

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\*The actual calculation is done on the energy, but we will conform to the accepted misuse of the word "force" in referring to them.

Rushbrooke [12]

$$W_{\ell L} = \sum_{i\rho} q_i q_\rho \sum_{\ell, L} \frac{r_i^{-\ell} r_\rho^L}{R^{\ell+L+1}} B_{\ell L} \sum_{m=-\alpha}^{+\alpha} \frac{Y_{\ell(i)}^{-m} Y_{\ell(\rho)}^m}{[(\ell+m)! (\ell-m)! (L+m)! (L-m)!]}^{1/2}, \quad (3)$$

where

$$B_{\ell L} = (-1)^\alpha \frac{4\pi(\ell+L)!}{\sqrt{(2\ell+1)(2L+1)}},$$

$\alpha$  is the smaller of  $\ell$  and  $L$ ,  $q$  is the electron charge,  $i$  and  $\rho$  are electrons on separate centers, and the  $Y_\ell^m$ 's are spherical harmonics. If we take the Z-axis along the internuclear axis and consider only the  $R^{-6}$  (dipole) part of the dispersion forces, this becomes (using atomic units)

$$W_d = \sum_{i\rho} w_{i\rho}, \quad (4)$$

where

$$w_{i\rho} = -\frac{8\pi}{3R^3} r_i r_\rho \Theta_{i\rho},$$

$$\text{and} \quad \Theta_{i\rho} = 1/2 Y_1^{-1}(i) Y_1^1(\rho) + Y_1^0(i) Y_1^0(\rho) + 1/2 Y_1^1(i) Y_1^{-1}(\rho).$$

Inter-atomic Equations.---In deriving the inter-atomic equations necessary to determine dispersion forces we follow the arguments of the Many-Electron Theory for atoms, using an appropriate two-center wavefunction and the exact Hamiltonian\*, equation (1),

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\*to use a perturbation-like form would be an unnecessary complication from a computational standpoint, as pointed out previously.



to arrive at the inter-atomic equivalent of equation (III:28).

However, since  $E_{HF}$  does not contribute to dispersion forces, we may deal with only  $E_R(\chi)$  at the outset. Equation (III:28) would then be written

$$E_R(\chi'_s) = \frac{2\langle \psi^0 | H_A + H_B + U | \chi'_s \rangle + \langle \chi'_s | H_A - E_A + H_B - E_B + U | \chi'_s \rangle}{1 + \langle \chi'_s | \chi'_s \rangle} \quad (5)$$

The principle difference between the present inter-atomic case and the preceding atomic discussion occurs in the choice of the correlation wavefunction  $\chi'_s$ . Following the same arguments as in the atomic case, correlations between pairs of electrons are presumed to be the major effect. However, now there are two types of pair functions: those representing intra-atomic pair correlations only, and those representing inter-atomic pair correlations only. Once a correlation wavefunction of this form is put into equation (5) the resulting expression can be treated in a Varied-Portions way and selected parts minimized. However, in the case of dispersion forces we are dealing with interactions (or energy contributions) that are very weak to begin with, so it is no longer necessarily true that the many-electron effects in the energy (triangles and higher order diagrams) are small relative to the pair interactions. In fact, one purpose of the calculation done here is to include the coupling of the two types of pairs in the minimized portion of equation (5). We now develop the specific equations corresponding to these general comments.

# VARIED-PORIONS RESULT FOR HELIUM-HELIUM

The wavefunction of two helium atoms interacting at large distances is written as

$$\Psi = \Psi^0 + \chi'_s, \quad (6)$$

where  $\Psi^0 = \psi_A^{\text{OO}} \psi_B^{\text{OO}}$ , a product of the Hartree-Fock wavefunctions of the separate atoms, and  $\chi'_s$  is given by

$$\chi'_s = \psi_A^{\text{OO}} \{\hat{u}_{\rho\nu}\} + \{\hat{u}_{ij}\} \psi_B^{\text{OO}} + \{\hat{u}_{ij} \hat{u}_{\rho\nu}\} + \sum_{i,\rho} \{\hat{u}_{i\rho}\} + \sum_{i,\rho} \{\hat{u}_{i\rho} \hat{u}_{j\nu}\} \quad . * \quad (7)$$

The first three terms are intra-atomic correlation wavefunctions and their unlinked cluster. The last terms are the inter-atomic interaction and include all such contributions.\*\* Now, remembering that we are only considering the dipole contribution to the dispersion force, which according to  $\Theta_{i\rho}$  of equation (4) involves  $Y_1^m$  spherical harmonics, we conclude that  $\{\hat{u}_{i\rho}\}$  for helium must also only include

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\*ij on center A,  $\rho\nu$  on center B.

$$**\{\hat{u}_{i\rho}\} = \alpha^A \alpha^B \{\Gamma(A;i) \Gamma(B;\rho) \hat{u}_{i\rho}\}$$

$$\{\hat{u}_{i\rho} \hat{u}_{j\nu}\} = \alpha^A \alpha^B \{\Gamma(A;ij) \Gamma(B;\rho\nu) \hat{u}_{i\rho} \hat{u}_{j\nu}\}$$

atomic p-orbitals. Furthermore, as Parr has shown [13], the coulomb integrals between two p-orbitals on separate centers follow an asymptotic expansion in  $R^{-1}$  at large separations. Using this we can easily show that the inter-atomic pair function at large separations behaves as  $R^{-3}$ . We will therefore later factor this dependence out of  $\{\hat{u}_{i\rho}\}$ .

To simplify notation let us define  $a = \langle \hat{u}_{12} | \hat{u}_{12} \rangle$ ,  $b = \langle \hat{u}_{34} | \hat{u}_{34} \rangle$ , and  $c = \sum_{i\rho} \langle \hat{u}_{i\rho} | \hat{u}_{i\rho} \rangle$ . Then when we put equation (7) into equation (5) the resulting expression for the interaction of two helium atoms is:

$$\begin{aligned}
 E_R(\chi'_s) = & \frac{[2\langle \psi_A^0 | g_{12} | \{\hat{u}_{12}\} \rangle + \langle \{\hat{u}_{12}\} | T^A - E_{HF}^A + g_{12} | \{\hat{u}_{12}\} \rangle] \times [1+a]}{1 + a + b + c + ab + \dots} \\
 & + \frac{[2\langle \psi_B^0 | g_{34} | \{\hat{u}_{34}\} \rangle + \langle \{\hat{u}_{34}\} | T^B - E_{HF}^B + g_{34} | \{\hat{u}_{34}\} \rangle] \times [1+b]}{1 + a + b + c + ab + \dots} \\
 & + \frac{\sum_{i\rho} [2\langle \psi_A^0 \psi_B^0 | w_{i\rho} | \{\hat{u}_{i\rho}\} \rangle + \langle \{\hat{u}_{i\rho}\} | T^A - E_{HF}^A + T^B - E_{HF}^B + g_{ij} + g_{\rho\nu} | \{\hat{u}_{i\rho}\} \rangle] \times [1+c]}{1 + a + b + c + ab + \dots} \\
 & + (\text{coupling terms and terms proportional to } R^{-n} \text{ for } n > 6), \quad (8)
 \end{aligned}$$

where electrons 1 and 2 are on center A, and 3 and 4 are on center B. Since we are using the exact Hamiltonian, the operators  $T^A$  and  $T^B$

are defined as

$$T^A = - \sum_i \left( \frac{1}{2} \nabla_i^2 + \frac{Z_A}{r_i} \right) , \quad (9)$$

$$T^B = - \sum_\rho \left( \frac{1}{2} \nabla_\rho^2 + \frac{Z_B}{r_\rho} \right) , \quad (10)$$

with  $E_{HF}^A$  and  $E_{HF}^B$  given by,

$$E_{HF}^A = \langle \psi_A^0 | T^A + g_{12} | \psi_A^0 \rangle \quad (11)$$

$$E_{HF}^B = \langle \psi_B^0 | T^B + g_{34} | \psi_B^0 \rangle . \quad (12)$$

Note that this expression contains parts which look like the pairs of the atomic case, except that here no Hartree-Fock operators appear. We use the exact Hamiltonian and identify pairs only by the appearance of a pair function in the wavefunction; it is not necessary to force the appearance of a pair-operator\* too. There are two intra-atomic pairs, four inter-atomic pairs, and coupling terms. The normalization terms, a and b, are much smaller than 1, and c vanishes as  $R^{-6}$  at large separations. It has been shown that under these circumstances the denominator will effectively cancel the normalization

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\*Such as the  $(e_i + e_j + m_{ij})$  of equation (III:40); also see footnote, page 45.

term in the numerator [3] so that a good approximation to equation (8) is given by

$$E_R(\chi'_s) = \frac{\epsilon_{12}}{1+a+c} + \frac{\epsilon_{34}}{1+b+c} + 4x \frac{\epsilon_{13}(R^{-6})}{1+a+b+c} + R, \quad (13)$$

where  $\epsilon_{12} = 2\langle Q_{12}(\varphi_1\varphi_2) | g_{12} | \{\hat{u}_{12}\} \rangle + \langle \{\hat{u}_{12}\} | T^A - E_{HF}^A + g_{12} | \{\hat{u}_{12}\} \rangle, \quad (14)$

$$\epsilon_{34} = 2\langle Q_{34}(\varphi_3\varphi_4) | g_{34} | \{\hat{u}_{34}\} \rangle + \langle \{\hat{u}_{34}\} | T^B - E_{HF}^B + g_{34} | \{\hat{u}_{34}\} \rangle, \quad (15)$$

$$\epsilon_{13}(R^{-6}) = 2\langle \psi_A^O \psi_B^O | w_{13} | \{\hat{u}_{13}\} \rangle + \langle \{\hat{u}_{13}\} | T^A - E_{HF}^A + T^B - E_{HF}^B + g_{12} + g_{34} | \{\hat{u}_{13}\} \rangle \quad (16)$$

and  $R = (\text{coupling terms and terms proportional to } R^{-n} \text{ for } n > 6). \quad (17)$

The factor of four arises because at the distances considered all four inter-atomic pair correlations are equivalent and only one needs to be calculated.

It would be clearer to visualize equation (13) in terms of two-center diagrams. These are constructed analogous to the earlier atomic diagrams. For helium we obtain from the above the following diagrams:

$$\epsilon_{12} = \begin{array}{cc} \textcircled{C} & \textcircled{\quad} \\ A & B \end{array} \quad (18)$$

$$\epsilon_{34} = \begin{array}{cc} \bigcirc & \bigcirc \\ A & B \end{array} \quad (19)$$

$$\epsilon_{13}(R^{-\epsilon}) = \begin{array}{cc} \bigcirc & \bigcirc \\ A & B \end{array} + \begin{array}{cc} \bigcirc & \bigcirc \\ A & B \end{array} + \begin{array}{cc} \bigcirc & \bigcirc \\ A & B \end{array} \quad (20)$$

$$\begin{aligned} \mathcal{R} = & \begin{array}{cc} \bigcirc & \bigcirc \\ A & B \end{array} + \begin{array}{cc} \bigcirc & \bigcirc \\ A & B \end{array} + \begin{array}{cc} \bigcirc & \bigcirc \\ A & B \end{array} \\ & + \begin{array}{cc} \bigcirc & \bigcirc \\ A & B \end{array} + \begin{array}{cc} \bigcirc & \bigcirc \\ A & B \end{array} + \dots \end{aligned} \quad (21)$$

where the dotted line now signifies  $r_{ij}^{-1}$  instead of  $m_{ij}$  because we are using the exact Hamiltonian. From this we see that  $\epsilon_{12}$  and  $\epsilon_{34}$  do not have any  $R$ -dependence and need not be considered further insofar as dispersion forces are concerned. Except for a minor normalization correction,

$$N = \left( \frac{\epsilon_{12}}{1+a} \right) \left( \frac{-c}{1+a} \right) + \left( \frac{\epsilon_{34}}{1+b} \right) \left( \frac{-c}{1+b} \right) \quad (22)$$

the only part we need concern ourselves with when applying the Varied-Portions Approach is  $\epsilon_{13}$  and  $\mathcal{R}$ .

Now, an important point is raised here. Note that there are contributions which contain parts not only behaving as  $R^{-6}$  but also as higher powers of  $R^{-1}$ . Since we wish to calculate only the dipole ( $R^{-6}$ ) contribution to the dispersion force, the Varied-Portions Approach minimizes only that part of  $(\epsilon_{13} + \mathcal{R})$  which behaves as  $R^{-6}$ . But, there is the question of whether this part is independent of effects which vary as higher powers of  $R^{-1}$ .

We can easily prove this by considering the complete  $E_R(\chi'_S)$ . If all multipole terms of  $U(R)$  had been considered, the total  $\epsilon_{13}$  would consist of the following contributions

$$\epsilon_{13} = \epsilon_{13}(\text{dipole-dipole}) + \epsilon_{13}(\text{dipole-quad.}) + \dots \quad (23)$$

Furthermore, since each of these multipole effects has a specific symmetry, there would be corresponding symmetry terms in the inter-atomic correlation wavefunction

$$\{u_{13}\} = \{u_{13}^{PP}\} + \{u_{13}^{Pd}\} + \dots \quad (24)$$

The first term represents a p-excitation on each center, the second a p-excitation on one center and a d-excitation (quadrupole) on the other, and so on. Then one finds in the expansion of equation (13) that all cross-terms between the various contributions vanish until terms of the form

$$\langle \{u_{13}^{PP}\} | w_{13}^{Pd} | \{u_{13}^{Pd}\} \rangle \neq 0 \quad (25)$$

occur. This produces the first symmetry-coupling effect and behaves as  $R^{-11}$ . Consequently, one is justified in treating not only  $R^{-6}$ , but also  $R^{-8}$  and  $R^{-10}$  interactions separately in the minimization process.

There is one final simplification possible if one considers the equivalence of inter-atomic pairs. In  $W_d$  and  $\Theta_{ip}$  of equation (4) one needs only to include one of the three terms, since the coefficients in  $\Theta_{ip}$  define the relative contributions of the other two. In later calculations we will use only the  $Y_1^0(i) Y_1^0(\rho)$  term.

If we define

$$R_{III}(R^{-6}) = \text{Diagram 1} \quad (26)$$

$$R_{IV}(R^{-6}) = \text{Diagram 2} \quad (27)$$

$$Q_I(R^{-6}) = \text{Diagram 3} \quad (28)$$

$$Q_{II}(R^{-6}) = \text{Diagram 4} \quad (29)$$



the total helium  $R^{-6}$  interaction is given by

$$E_R(R^{-6}) = \frac{4\epsilon_{13} + 8R_{III} + 16R_{IV} + 8Q_I + 8Q_{II}}{1 + a + b} + 4N, \quad (30)$$

where the coefficients are simply those necessary to insure that the proper numbers of each diagram are included. In the calculations described next, the Varied-Portions Approach is applied to this equation.

## V. HELIUM-HELIUM CALCULATION

### COMPUTATIONAL DETAILS

We now describe a calculation based on equation (III:23) to obtain the  $R^{-6}$  energy contribution to the dispersion "forces" between two helium atoms. This equation gives the total  $R^{-6}$  interaction as

$$E_R(R^{-6}) = 4X \frac{\epsilon_{24} + 2R_{III} + 4R_{IV} + 2Q_I + 2Q_{II}}{1 + a + b} + 4N, \quad (1)$$

where the four is factored out because all four inter-atomic pairs are equivalent at the distances considered; only one, here designated as the 2,4 pair, needs to be calculated. The quantity

$$\tilde{J} = \epsilon_{24} + 2R_{III} + 4R_{IV} + 2Q_I + 2Q_{II} \quad (2)$$

is then treated in a Varied-Portions Approach and the following three segments made stationary:

- I.  $\epsilon_{24}$  only
- II.  $\epsilon_{24} + 2R_{III}$
- III.  $\epsilon_{24} + 2R_{III} + 4R_{IV}$  .

After the variational problem is solved, the normalization correction and other terms left out at each of these stages are then computed

and added in to get the total  $R^{-6}$  energy.

The many-electron wavefunctions are constructed from one-electron spin orbitals. Their spatial part is defined as

$$\varphi_{\alpha\ell m}(r\theta\varphi) = P_{\alpha\ell}(r)Y_{\ell}^m(\theta\varphi) \quad (3)$$

where  $\ell$  and  $m$  denote the symmetry species and sub-species respectively, and  $\alpha$  labels orbitals not distinguishable by symmetry alone. The radial function is expanded in terms of a normalized Slater type basis set,

$$P_{\alpha\ell}(r) = \sum_p c_{\alpha\ell p} R_{\ell p}(r) \quad (4)$$

with

$$R_{\ell p}(r) = \left[ \frac{(2\xi_{\ell p})^{2n_{\ell p}+1}}{(2n_{\ell p})!} \right]^{1/2} r^{n_{\ell p}-1} e^{-\xi_{\ell p} r}, \quad (5)$$

where  $n_{\ell p}$  is the quantum number of the Slater function. These functions are normalized such that,

$$\int_0^{\infty} P_{\alpha\ell}(r) P_{\alpha'\ell}(r) r^2 dr = \delta_{\alpha\alpha'}, \quad (6)$$

$$\int_0^{\infty} R_{\ell p}(r) R_{\ell p'}(r) r^2 dr = \delta_{pp'}, \quad (7)$$

The spin orbital is obtained by multiplying the spatial orbitals by either an  $\alpha$  or  $\beta$  spin function. A  $\beta$ -spin orbital is distinguished from an  $\alpha$ -spin orbital by a bar,

$$\varphi_{\alpha\ell m}(i) \beta(i) = \bar{\varphi}_{\alpha\ell m}(i) \quad (8)$$

$$\varphi_{\alpha\ell m}(i) \alpha(i) = \varphi_{\alpha\ell m}(i) \quad . \quad (9)$$

From these spin orbitals each part of the wavefunction in equations (IV:6) and (IV:7) is constructed as a linear combination of Slater determinants with coefficients chosen to satisfy the symmetry requirements for each particular part. The symmetry of the ground states of each atom is taken to be  $^1S$ , so the uncorrelated part of the wavefunction for the interacting system is just a product of  $^1S$  single Slater determinants,

$$\Psi^0 = \alpha^A(\varphi_{100}(1) \bar{\varphi}_{100}(2)) \alpha^B(\varphi_{100}(3) \bar{\varphi}_{100}(4)) \quad , \quad (10)$$

where the first two electrons are on center A and the second two on center B. Since the overlap is presumed negligible, antisymmetry between centers is not required.

The intra-atomic correlation part of  $\chi'_s$  for each center must also be  $^1S$  symmetry. We can write for center A,

$$\{\hat{u}_{ij}\} = \sum_k C_K \Psi_K + \Omega \quad (11)$$

where the  $\Psi_K$  are all those  $^1S$  linear combinations of Slater determinants constructed from only  $\ell = 1$  orbitals. The  $\Omega$  then contains all other linear combinations of Slater determinants and is also  $^1S$  symmetry. The  $C_K$  are the configuration mixing coefficients which must be determined by a calculation on a single atom. A typical  $\Psi_K$  would be given by

$$\frac{1}{\sqrt{3}} [-C^A(\varphi_{111}(1)\bar{\varphi}_{1\bar{1}\bar{1}}(2)) + C^A(\varphi_{110}(1)\bar{\varphi}_{110}(2)) - C^A(\varphi_{1\bar{1}\bar{1}}(1)\bar{\varphi}_{111}(2))]. \quad (12)$$

For center B one would have identical functions.

The inter-atomic correlation part of the wavefunction need only satisfy the symmetry of the perturbation,  $^{\oplus}_{1\rho}$ . Since we have already established that the  $R^{-6}$  interaction involves p-excitations, only  $\ell = 1$  spin orbitals are used to construct the Slater determinants in this part. The consequence of this is that the  $\Omega$  part of  $\{\hat{u}_{ij}\}$ , equation (11), will not mix with the inter-atomic correlated wavefunction and can be neglected. Furthermore, one does not even need all of  $\Psi_K$ . Since the relative contributions of the determinants are defined by the square of the coefficients in  $^{\oplus}_{1\rho}$ , see equation (IV:4), we choose to use only the  $\frac{1}{\sqrt{3}} [C^A(\varphi_{\alpha 1 0}(1)\bar{\varphi}_{\alpha 1 0}(2))]$  part of each  $\Psi_K$ . The energy obtained at each of the three stages will then have to be multiplied by 3/2 to get the total energy. Therefore, the configurations used to account for intra-atomic correlation on atom A were,\*

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\*Antisymmetry within parenthesis is implied and electron numbering omitted from now on.

1.  $\frac{1}{\sqrt{3}} (\varphi_{110} \bar{\varphi}_{110})$
2.  $\frac{1}{\sqrt{3}} (\varphi_{210} \bar{\varphi}_{210})$
3.  $\frac{1}{\sqrt{3}} (\varphi_{310} \bar{\varphi}_{310})$  ;

and, identical configurations were used for atom B.

The six configurations used in this calculation to account for inter-atomic correlation were (for a 2,4-pair),

$$1. (\varphi_{100} \bar{\varphi}'_{110}) (\varphi_{100} \bar{\varphi}'_{110}) \quad (13)$$

$$2. (\varphi_{100} \bar{\varphi}'_{210}) (\varphi_{100} \bar{\varphi}'_{210}) \quad (14)$$

$$3. (\varphi_{100} \bar{\varphi}'_{310}) (\varphi_{100} \bar{\varphi}'_{310}) \quad (15)$$

$$4. (\varphi_{100} \bar{\varphi}'_{110}) (\varphi_{100} \bar{\varphi}'_{210}) + (\varphi_{100} \bar{\varphi}'_{210}) (\varphi_{100} \bar{\varphi}'_{110}) \quad (16)$$

$$5. (\varphi_{100} \bar{\varphi}'_{110}) (\varphi_{100} \bar{\varphi}'_{310}) + (\varphi_{100} \bar{\varphi}'_{310}) (\varphi_{100} \bar{\varphi}'_{110}) \quad (17)$$

$$6. (\varphi_{100} \bar{\varphi}'_{210}) (\varphi_{100} \bar{\varphi}'_{310}) + (\varphi_{100} \bar{\varphi}'_{310}) (\varphi_{100} \bar{\varphi}'_{210}) . \quad (18)$$

It is important to note at this point that, although  $\ell = 1$  orbitals are used in both the intra-atomic and inter-atomic parts, these orbitals are different from each other, as distinguished by the prime

on the latter. Inter-atomic correlation involves electron density more in the outer regions of the atom, whereas intra-atomic correlation takes place more in the inner regions. Consequently, intra-atomic correlation orbitals are not suitable for describing inter-atomic correlation.

The total wavefunction is constructed by adding together all the above parts with their mixing coefficients to give

$$\Psi = C_0 \Psi^0 + \psi_A^0 \left( \sum_{\rho=1}^3 C_{\rho} \Psi_{\rho} \right) + \left( \sum_{i=1}^3 C_i \Psi_i \right) \psi_B^0 + \sum_{K=1}^6 D_K \mu_K + (\text{unlinked clusters}) \quad (19)$$

where the  $\Psi_i$  and  $\Psi_{\rho}$  are the intra-atomic single Slater determinants with their symmetry coefficient, i.e.,  $\frac{1}{\sqrt{3}}$  and the  $\mu_K$  are the inter-atomic configurations in equations (13) - (18). Including the unlinked clusters introduces no new mixing coefficients. For instance, in an intra-atomic unlinked cluster a typical term is,

$$C_i C_{\rho} \Psi_i \Psi_{\rho} \quad (20)$$

while in an inter-atomic unlinked cluster a typical term is,

$$D_J D_K \mu_J \mu_K \quad (21)$$

For the  $\Psi^0$  orbitals we used the Bagus-Gilbert basis set [14] defined in Table I. The intra-atomic mixing coefficients and orbitals

were taken from Sabelli and Hinze's multiconfigurational calculation of the correlation energy of the helium atom [15]. Their coefficients had to be renormalized for our calculation, since our theory requires  $C_0 = 1$ . Using the results of their final calculation, an exact pair calculation of the correlation energy of the helium atoms was carried out using all of their configurations except those involving f-orbitals. A value of  $-0.0407$  a.u. was found. Since the S + P + D limit for the correlation energy is considered to be  $-0.0410$  a.u. [16], these intra-atomic mixing coefficients and orbitals were considered to be optimum and they remained fixed throughout our calculation. In Table III we list the coefficients needed from Sabelli and Hinze's work, renormalized.

The inter-atomic mixing coefficients and exponents for the inter-correlated orbitals were determined in our calculation. We constructed each of these orbitals with only one Slater type function. Since the correlation energy was found to be rather insensitive to the orbital exponents, they were determined once and for all at stage I. Table IV lists our basis set and Table V contains the inter-atomic mixing coefficients obtained at each stage in the calculation. The results for the  $R^{-6}$  interaction obtained from the three stages of the calculation are summarized in Tables VI - VIII.



TABLE I  
Bagus-Gilbert Basis Set

A. Coefficients	B. Exponents	C. Quantum Number
$c_{101} = 1.3621$	$\xi_{01} = 1.450$	$n_{01} = 1$
$c_{102} = -0.10724$	$\xi_{02} = 2.641$	$n_{02} = 2$
$c_{103} = -0.28189$	$\xi_{03} = 1.723$	$n_{03} = 2$

TABLE II  
Hinze p-orbital Basis Set for  $\varphi_{\alpha 10}$

A. Coefficients		
$c_{111} = 1.24659$	$c_{211} = 2.44713$	$c_{311} = 2.22774$
$c_{112} = -0.31378$	$c_{212} = -1.74540$	$c_{312} = 0.29186$
$c_{113} = 0.04570$	$c_{213} = -0.43626$	$c_{313} = 2.44204$
$c_{114} = 0.00070$	$c_{214} = -0.56693$	$c_{314} = -4.88266$
B. Exponents		C. Quantum numbers
$\xi_{11} = 2.5834$		$n_{11} = 2$
$\xi_{12} = 3.6413$		$n_{12} = 2$
$\xi_{13} = 5.5308$		$n_{13} = 3$
$\xi_{14} = 5.7217$		$n_{14} = 4$

TABLE III

Hinze Configuration Mixing  
Coefficients (renormalized)

$C_1 = -.06212$
$C_2 = -.01085$
$C_3 = -.00263$

TABLE IV

Our Basis Set for  $\varphi'_{\alpha 10}$

A. Coefficients		
$c_{111} = 1.00000$	$c_{211} = 0.00000$	$c_{311} = 0.00000$
$c_{112} = 0.00000$	$c_{212} = 1.00000$	$c_{312} = 0.00000$
$c_{113} = 0.00000$	$c_{213} = 0.00000$	$c_{313} = 1.00000$
B. Exponents	C. Quantum numbers	
$\xi_{11} = 1.285$	$n_{11} = 2$	
$\xi_{12} = 1.500$	$n_{12} = 3$	
$\xi_{13} = 1.500$	$n_{13} = 4$	

TABLE V  
Inter-atomic Configuration  
Mixing Coefficients

	1	2	3	4	5	6
Stage I	0.34844	0.08235	0.01827	0.00501	-0.03845	-0.01212
Stage II	0.30119	0.10064	0.02066	0.00959	-0.03666	-0.016135
Stage III	0.26488	0.09062	0.01933	0.01995	-0.03223	-0.01436

TABLE VI  
The  $R^{-6}$  Coefficient Obtained  
at Stage I

4 $\epsilon_{24}$	-1.6640 a.u.
8 $R_{III}$	.1227
16 $R_{IV}$	.1734
Total	-1.3679

TABLE VII  
The  $R^{-6}$  Coefficient Obtained  
at Stage II

$4 \epsilon_{24} + 8R_{III}$	-1.5506 a.u.
$16R_{IV}$	.1607
Total	-1.3899

TABLE VIII  
The  $R^{-6}$  Coefficient Obtained  
at Stage III

$4 \epsilon_{24} + 8R_{III} + 16R_{IV}$	-1.3948 a.u.
$8Q_I$	-0.0013
$8Q_{II}$	-0.0011
	-1.3972
Renormalized ( $1 + a + b = 1.0161$ )	-1.3751
$4 N$	.0508
Total	-1.3243

TABLE IX  
Wahl Basis Set for  $\varphi'_{\alpha 10}$

A. Coefficients	
$c_{111} = 1.00000$	$c_{211} = 0.00000$
$c_{112} = 0.00000$	$c_{212} = 1.00000$
B. Exponents	C. Quantum numbers
$\xi_{11} = 1.90$	$n_{11} = 2$
$\xi_{12} = 1.45$	$n_{12} = 2$

TABLE X  
Schaefer Basis Set for  $\varphi'_{\alpha 10}$

A. Coefficients	
$c_{111} = 1.00000$	$c_{211} = 0.00000$
$c_{112} = 0.00000$	$c_{212} = 1.00000$
B. Exponents	C. Quantum numbers
$\xi_{11} = 1.60$	$n_{11} = 2$
$\xi_{12} = 1.60$	$n_{12} = 3$

TABLE XI  
Schaefer and Wahl Mixing Coefficients\*

	$D_1$	$D_2$	$D_3$
Schaefer	.09469	.15414	.05310
Wahl	.13049	.74170	-.27589

\*Their  $D_1$ ,  $D_2$ , and  $D_3$  configurations are constructed the same as our  $D_1$ ,  $D_2$ , and  $D_4$  configurations equations (13), (14), and (16).

## DISCUSSION

This calculation is the first to obtain the four-electron contributions,  $Q_I$  and  $Q_{II}$ , to the dispersion interaction. Although they were small as predicted, it is necessary to include them to obtain an upper bound to  $C_6^*$ ; our value is found in Table VIII. Also, this is the only Many-Electron Theory calculation of dispersion forces that allowed both exponential and linear variations in the wavefunction when the energy was made stationary. The single previous work of this type [17] used only linear parameters. In particular, the orbitals used there to account for electron correlation were expressed as a power series in the electronic coordinate times the zero-order Hartree-Fock orbital. Since it requires a large number of terms (reference [17] used only three) in such a series before linear variation will affect the electron density as much as the variation of a single exponent, there existed some question as to whether this earlier calculation adequately accounted for electron correlation. Our calculation does not suffer from this objection, and we will later elaborate on the roles of intra-atomic and inter-atomic correlation in dispersion force calculations.

We also had as a major aim the development of a computer program with broad capabilities in the area of dispersion force calculations. The one produced and used here is quite general and designed to automatically "construct" from a given set of configurations

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\*The dispersion interaction coefficients will be referred to as  $C_6$ ,  $C_8$ , and  $C_{10}$ .

all the diagrams arising in the theory. It then introduces anti-symmetry on each center and computes all integrals associated with each diagram. Thus, one can either sum all possible diagrams to get the total interaction, or extract specific diagrams to study any part of the interaction. By having access to each type of diagram one can take full advantage of the independence of the  $R^{-6}$ ,  $R^{-8}$ , and  $R^{-10}$  interactions because one can easily calculate only those diagrams contributing to the interaction of interest.\* Extension of the theory to higher order interactions and larger systems is now quite simple, and efforts in this direction are already underway.

But, the primary purpose of this work was the development of the theory itself. Previous calculations of dispersion force coefficients all suffered from one or another inherent theoretical complication. Our intention here was to evolve an electron correlation theory of dispersion forces that was both simple to apply and yet completely rigorous at all stages. That a new approach was warranted is evident if one considers the difficulties of earlier methods.

Molecular orbital methods using configuration-interaction wavefunctions are one type of calculation frequently used to study the interaction of two atomic or molecular systems. They treat the total energy of the system and are usually concerned with the interaction at all separations. Then, when the calculation is extended into the region of negligible overlap, the  $R^{-6}$ ,  $R^{-8}$ , and  $R^{-10}$

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\*All calculations were done in double precision on an IBM 360/65.



dispersion interactions do not emerge as independent; consequently, the dispersion coefficients are not explicitly produced. They can be obtained from these types of calculations in an approximate way, but the values are never true bounds to the interaction. Furthermore, a large number of configurations are necessary, leading to computations far more difficult than necessary for long-range interactions.

As a matter of interest, though, and as an intermediate check on our work, we studied two such calculations, one by P. Bertocini and A. Wahl [18] and the other by H. F. Schaefer, et al. [19], neither of which took intra-atomic correlation into account. By using their configurations in our program we were able to vary the configuration mixing coefficients to make  $\epsilon_{24} + 2 \nabla$  stationary and thus extract  $R^{-6}$  coefficients using their basis functions. The values obtained,  $-1.5479^*$  from Wahl and  $-1.5481$  from Schaefer, are still not true bounds, but they do represent the  $R^{-6}$  coefficient obtainable from their basis set. The basis sets and mixing coefficients for these calculations are found in Tables IX - XI. We point out that this analysis is identical to our stage II calculation, except that we used a more extensive set of configurations. For comparison our stage II result was  $-1.5506$ , indicating close agreement at this point between our method and the more extensive calculations. Schaefer had estimated that his calculation had a  $C_6$  of  $-1.57$ .

Another common type of dispersion force calculation is

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\*All values will be quoted in atomic units in this discussion.

based on perturbation theory, both time-dependent and time-independent. The time-dependent approach is just the one-center method already discussed at length in Part I. It has the advantage of not needing the intra-atomic correlation wavefunction, but it results in a very detailed computation. Many frequency-dependent polarizabilities must be calculated in order to obtain the dispersion coefficients. This is compounded by the necessity to define and treat Hartree-Fock operators in the calculation. Even though we have shown that using a commuting potential to simplify the equations should still yield good long-range dispersion interactions, the computer time required of this method is still several times what is required with our approach. Its results for helium do not indicate it is any more accurate. The time-independent approach using the total Hamiltonian of each atom has yielded a very accurate value for  $C_6$  of helium, but it requires knowledge of the exact zero-order wavefunction of the system, and so is useless for other systems. It is interesting to note that the usual value attributed to Davison's work [20],  $-1.47$  a.u., violates the variational principle since the more recent estimated value for the helium  $C_6$  is  $1.4618 \pm .0004$  [21]. The number that should be quoted from his work is  $-1.4586$ ; the  $-1.47$  was obtained by scaling his polarizability before calculating the total  $R^{-6}$  interaction.


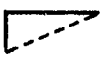
The last type of calculation, of which there is only one [17], is based on a pair correlation theory, but still suffers from the necessity of defining Hartree-Fock operators in a variational theory.

Besides compounding the difficulty as in perturbation theories, their presence introduces a certain lack of rigor in a pair theory. This arises from the appearance of the self-potential terms in the Hartree-Fock potential. Since there is no unique, rigorous way to define pair energies which include self-potential terms,\* they must somehow be shuffled out of the portion of the energy minimized. Even though a scheme can be devised to accomplish this, as in reference [17], it is better to remove this arbitrariness altogether.

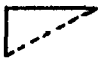
To avoid the above difficulties the simpler and more rigorous theory used here was developed. The groundwork was actually laid in Part I of this work. There, in conjunction with the Varied-Portions Approach, it was demonstrated that the appearance of Hartree-Fock-like operators is really quite arbitrary. Fully appreciating this fact allowed us to develop the theory in such a manner that the need to define them never arose; the earlier pair correlation calculation [17], although also a variational method, never really made this clean break with Hartree-Fock-like operators. But, we point out that this rather simple observation was more than a matter of semantics. In the case of the one-electron properties studied in Part I, it led to a unique and powerful theoretical tool; here, we have used it to produce an approach to dispersion forces which is both better defined theoretically and simpler to use computationally than previous methods.

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\*For instance in a four-electron problem, there are six pairs but only four self-potential terms.

The numerical results of this computation are found in Tables VI through VIII. The final  $R^{-6}$  coefficient in Table VIII represents an upper bound, but the values obtained from stage I and II, Tables IV and VII, do not include normalization or four-electron effects and therefore do not represent true bounds to the  $R^{-6}$  coefficient. Neither does the unnormalized value of stage III, the -1.3948 value in Table VIII, for the same reasons. But, a comparison of these values does indicate the relative importance of two types of pair coupling. The first type is coupling of two inter-atomic pairs represented by the  terms, and the second type is the coupling of an intra-atomic pair with an inter-atomic pair represented by the  terms. From stage I we see that the total three-electron contribution from both types of coupling is about 21 per cent, with the first terms contributing about 9 per cent and the second about 12 per cent. This is a significant contribution to the total, and some improvement can be expected if these coupling terms are included in the minimized portion of the total  $R^{-6}$  energy. In stage II we included the inter-inter coupling and realized a 1.6 per cent improvement over the result in stage I; but, when the intra-inter coupling was included in stage III, only an additional .3 per cent improvement was found.

The relative size of these improvements is a consequence of the fact that intra-atomic correlation and inter-atomic correlation occur in different regions of the atom, a point we made earlier in discussing the orbital basis sets used to describe the two types of

correlation. The intra-atomic pairs are already very nearly decoupled from the inter-atomic pairs at the outset, and including their coupling term, the , would not be expected to improve the energy greatly. However, that is not true of two inter-atomic pairs. If their coupling term is left out of the minimization step the two inter-pairs, in acting independently, will tend to occupy the same region of space. This obviously couples them very strongly. Since inter-inter coupling terms are positive, including them in the minimization step allows the two inter-pairs, in adjusting for each other's presence, to reduce their mutual interference and significantly improve the energy. This effect is also apparent in the size of the total inter-atomic overlap given by,

$$\sum_{K,J} \langle D_K \Psi_K | D_J \Psi_J \rangle \quad .$$

In going from stage I to stage II this overlap decreased from .1328 to .1166, about 12 per cent, but in going to stage III the reduction is less. Thus, allowing the pairs to couple in the variational process not only improves the minimum found when the energy is made stationary, but also reduces the normalization corrections that later must be made to obtain a true upper bound.

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## VITA

Bert R. Riemenschneider was born at San Antonio, Texas, on April 5, 1940. He attended Thomas Jefferson High School, and graduated May, 1958. He received his B.A. in chemistry from the Rice University, Houston, Texas, in 1962. He entered the Graduate School of the Louisiana State University in September 1967, where he is presently a candidate for the Doctor of Philosophy Degree.

He is married to the former Suellen Deage, also of San Antonio, and has a daughter, Terry Sue, born July 4, 1964.

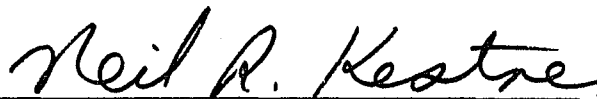
## EXAMINATION AND THESIS REPORT

Candidate: Bert R. Riemenschneider

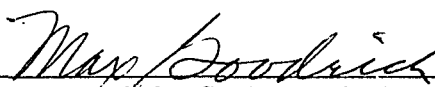
Major Field: Chemistry

Title of Thesis: I. Varied-Portions Approach to Second-Order Properties. II.  
Long-Range Interaction of Helium Atoms; Study of Three and Four  
Electron Correlation Effects

Approved:

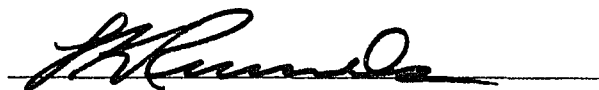


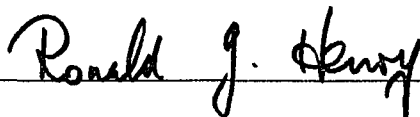
Major Professor and Chairman

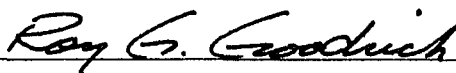


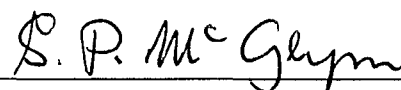
Dean of the Graduate School

### EXAMINING COMMITTEE:









Date of Examination:

November 9, 1971